

## Grant Information

Grant Number	HR0011-09-1-0047
Title of Research	Nanoscale Engineering of Multiferroic Hybrid Composites for Micro- and Nano-scale Devices
Principal Investigator	Dr. Charles J. O'Connor
Organization	University of New Orleans, New Orleans, LA 70148

## Final Technical Report September 14, 2012

### 1. Objectives:

- Develop a synthetic technology of lead-free high frequency multiferroic composites
- Develop a method of fabrication of arrays of free-standing magnetoelectric or multiferroic composites.
- Investigate wet chemistry synthesized multiferroic nanomaterials (nanoparticles, nanowires, nanotubes, etc.) using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to study their correlation between morphologies, composition, assembly, etc. and synthesis conditions. Meanwhile, e-beam *in-situ* nanolithography has been developed for multiferroic related devices fabrication.
- Fabricate spinel and perovskite pristine phases with controllable composition and dimensionality and use them as building blocks to design magnetoelectric ceramic nanocomposites with integrated functionalities
- Demonstrate that the direct ME effect can be measured at nanometer-length scale by detecting the changes in the piezoresponse of a multiferroic material when subjected to the action of a magnetic field.
- Mapping of the ME coupling through the domain imaging,
- Estimate quantitatively the ME coupling coefficient
- Understand the fundamental physics of magnetoelectric interactions at nanoscale for implementation of multiferroic materials into functional devices.

**Co-PI: Dr. Leszek Malkinski w/ Postdoc Dr. N. Babu**

### Brief Narrative:

Some of major problems with applications of multiferroic composites are: lead content, relatively large losses at microwave frequencies and a clamping effect. Therefore, our group research was focused on technology of new lead-free multiferroic composites suitable for high-frequency applications and on design of thin film materials which minimizes the stray effect of clamping of the composite by the substrate.

## Research Progress:

To realize the first objective a series of NBT-CFO ( $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3/\text{CoFe}_2\text{O}_4$ ) granular

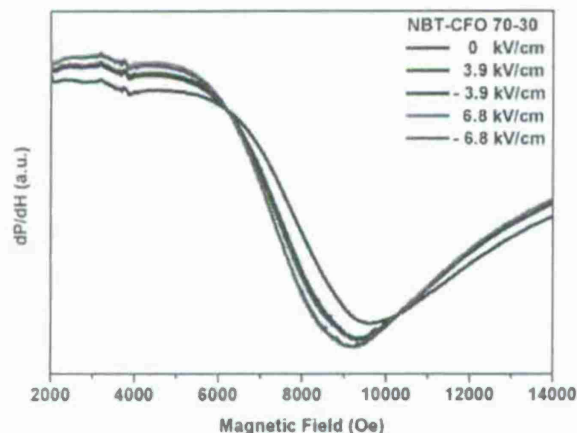


Fig.1. Ferromagnetic resonance curves of Co-ferrite in granular composites measured at different electric fields

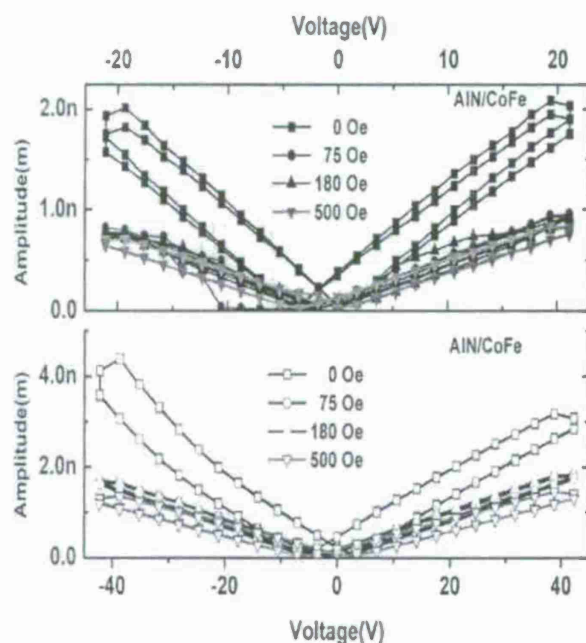


Fig. 2. The piezoelectric response amplitude variations with applied bias magnetic field, with driving voltage of  $V = 622.4$  and  $642.24$  V, for AlN/CoFe bilayer

multiferroic composites with 0-3 connectivity have been prepared by solid state sintering method. The volume fraction of the of the piezoelectric phase varied from 55% to 85%. The magnetic and piezoelectric properties as well as magnetoelectric properties have been carefully characterized. A record number of converse magnetoelectric coefficient of  $109 \text{ Oe cm/kV}$  was found in the sample with intermediate (30%) content of Co-ferrite [publications 3,5]. The effect of the electric field on ferromagnetic resonance curves is presented in Fig.1. In the case of laminate structures we proposed to use AlN as a piezoelectric phase [publication

4]. Although commonly used Pb-based PZT has superior piezoelectric performance it shows much larger losses at microwave frequencies than AlN. We fabricated bi-layer aluminum nitride (AlN)/cobalt iron (CoFe) magnetoelectric (ME) thin films using reactive rf/dc magnetron sputtering. The bi-layer thin film exhibited both good piezoelectricity and ferromagnetism, as well as ME effect. A 52% change observed in the piezoelectric signal (Fig.2.), measured using magnetic field assisted piezoresponse force microscopy, can be ascribed to the existence of a stress-mediated magnetoelectric coupling between AlN and CoFe. Finally, in order to reduce or eliminate the clamping effect in magnetoelectric composites we used stress engineering to fabricate free-standing magnetoelectric composites in the form of double microtubes [publication 4]. We used a new type of sacrificial layer (copper) to grow galfenol/aluminum/nitride films with 5 nm Au protective layers. The growth-induced stresses between GaFe and AlN layers caused rolling of the rectangular film patterns

when they were released from the sacrificial layer by selective etching of the Cu underlayer. The optical image of the array of the scrolled magnetoelectric film patterns



and the scanning electron microscope image of the magnified single structure are illustrated in Fig.3.

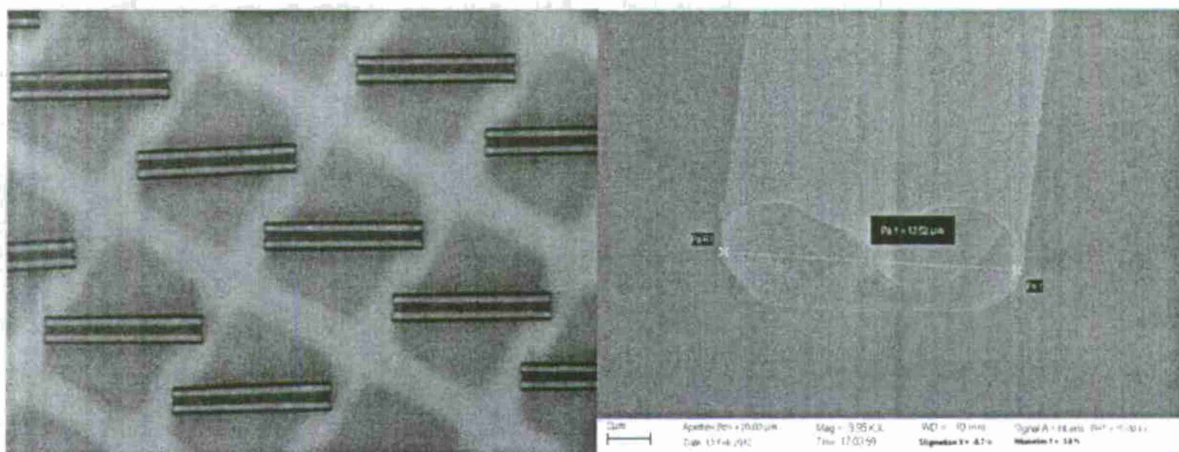


Fig.3. An array of "double barreled shotgun" magnetoelectric structures Au(5 nm)/AlN(20 nm)/CoFe(40 nm)/Au(5 nm) (SEM image of the tube on the right)

The research on multiferroic composites resulted in a discovery of a new biomedical application of multiferroic nanoparticles. This concept was a subject of UNO Technology disclosure and was published as a book chapter [publication 1]. Co-PI received additional funding from NSF EAGER grant to continue research on this problem.

**Co-PI: Dr. Weillie Zhou**

### Research Progress:

1. We observed free-standing, cubic-like monodispersed BaTiO<sub>3</sub> nanocrystals with well-defined shape, controllable size and a high degree of compositional homogeneity, which are essential for the study of the ferroelectricity at nanoscale, as well the possibilities to assemble individual nanoparticles into functional nanostructures, such as 3D ferroelectric crystals and magnetoelectric multiferroic superlattices.
2. In-situ nanolithography and measurement techniques under a field emission scanning electron microscope (FESEM) have attracted significant attention of many researchers since they provide facile ways to precisely pattern nanostructures for specific device fabrication, and measure the various characteristics (e.g. electrical and mechanical properties) of nanostructures without complicated sample preparation, respectively. In this work, in-situ nanolithography technique has been developed with great positioning accuracy for nanodevice fabrication. The positioning errors can be minimized to about 10 nm even without a high precision SEM stage, which is sufficient for most device fabrication. The simplified process can provides an easy, low cost and

less time consuming route to integrate nanomaterials based structures using a converted FESEM e-beam system.

**Co-PI: Dr. Gabriel Caruntu**

**Brief Narrative:**

The magneto-electric effect that occurs in some multiferroic materials is fully described by the magneto-electric coupling coefficient induced either electrically or magnetically. This is rather well understood in bulk multiferroics, but it is not known whether the magneto-electric coupling properties are retained at nanometer length scales in nano-structured multiferroics. The main challenges are related to measurement difficulties of the coupling at nanoscale, as well as the fabrication of suitable nano-multiferroic samples. Addressing these issues is an important prerequisite for the implementation of multiferroics in future nanoscale devices and sensors. In this paper we report on the fabrication of two ceramic nano-composite multiferroic samples with a perovskite as the ferroelectric phase and two different ferrites (cubic spinel and hexagonal) as the magnetic phases. The measurement of their magneto-electric coupling coefficients at nanoscale has been performed using a magnetic field-assisted piezoelectric force microscopy technique. The experimental data has been analyzed using a theoretical relation linking the piezoelectric coefficient to the magneto-electric coupling coefficient. Our results confirm the presence of a measurable magneto-electric coupling at nanoscale. The reported values as well as our theoretical approach are both in good agreement to previously published data for bulk and nanostructures magnetoelectric multiferroics.

**1. Research Progress:**

The PFM phase contrast image of the bilayered structure without poling the sample (Figure 2a) reveals the existence of randomly distributed bright and dark areas corresponding to parallel and antiparallel orientation of the polarization mapped by the piezoelectric response due to the tensor element  $d_{33}$  associated with ferroelectric domains all across the film surface ( $3 \times 3 \mu\text{m}^2$ ). As it can be noticed from the phase contrast images of the out-of-plane piezoresponse, when the magnetic applied field is varied from  $H = -600$  Oe to  $+600$  Oe the dark areas, which correspond to electric dipoles oriented downward, nucleate and grow at the expense of domains where polarization is oriented to the film surface (bright areas). This result suggests that the polarization can be switched in an opposite direction when an in-plane magnetic field is applied to the PTO-NFO bilayered nanocomposite as the result of a stress-mediated ME coupling between the ferrite and the perovskite layers. Figure 4 shows the phase and amplitude plots of the piezoresponse corresponding to the PTO-NFO bilayered structure in applied magnetic field. The amplitude signal displays the well-known "butterfly"-type aspect characteristic of a ferroelectric material. Figure 3a indicates that the piezoresponse phase hysteresis loops change their orientation at magnetic applied fields larger than 600 Oe. The change of  $179^\circ$  of the phase signal when the bias voltage



was swept from -22 to +22 V is associated with the existence of  $180^\circ$  domain structures in the PTO layers. The dominance of  $180^\circ$  domain structures of the dielectric dipoles in

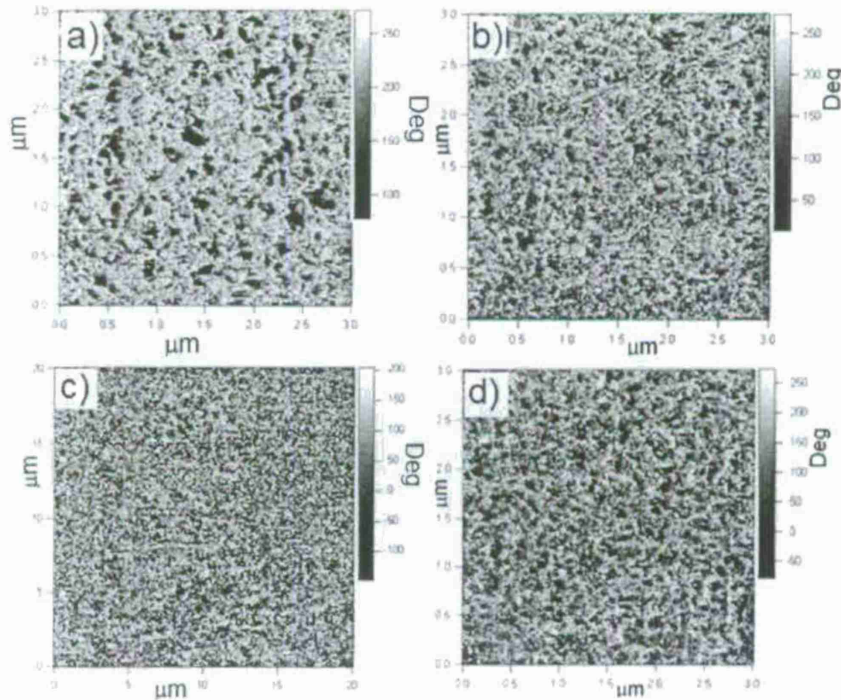


Figure 4. Piezoresponse images of the PTO-NFO bilayered composite under a magnetic field parallel to the plane of the film and different magnitudes  $H = -600$  Oe (a),  $0$  Oe (b),  $+300$  Oe (c) and  $+600$  Oe (d), respectively

the out-of-plane direction is also suggested by the linearity of the amplitude loops of the piezoelectric signal. The hysteresis loops are asymmetric with respect to the origin, presumably due to a small imprint [1-3], the different barrier potential between the electrode and the film [4], pinning of the domain walls by defects [3] or the presence of an internal electric field inside the film[5]. Moreover, the phase loops are shifted when the magnetic field is increased from  $0$  to  $2000$  Oe, but their variation is

random, similar to the case described recently by Xie and coworkers for CFO-PZT core-shell nanofibers[6]. Since the phase of the piezoresponse is related to the orientation of the ferroelectric domains, we can reasonably ascribe this change in the orientation of the phase hysteresis loops to the polarization change of the  $\text{PbTiO}_3$  layer due to the stress produced by adjacent ferrite layer at a critical value of the applied magnetic field. The phase curves are asymmetric with respect to the zero bias line (Figure 5a), being shifted to negative values with coercivities for the local switching of  $9.1$ ,  $9.7$ ,  $7.7$ ,  $9.9$ ,  $7.9$  and  $7.4$  V, respectively. The amplitude curves displayed in Figure 5b show a hysteretic behavior and their becomes steeper when the magnetic field was swept from  $0$  to  $2000$  Oe, thereby suggesting that the piezoelectric coefficient of the PTO-NFO bilayered nanocomposites is magnetic field dependent.

In order to rule out possible experimental artifacts, a PTO test-layer deposited under the same conditions on the  $\text{LaNiO}_3$ -buffer (100) was probed by PFM in applied magnetic field. No noticeable change of the slope of the measured piezoresponse amplitude has been detected, which confirms that such behavior is intrinsic, being the result of the electromechanical coupling between the magnetostrictive and piezoelectric layers in the nanocomposite.

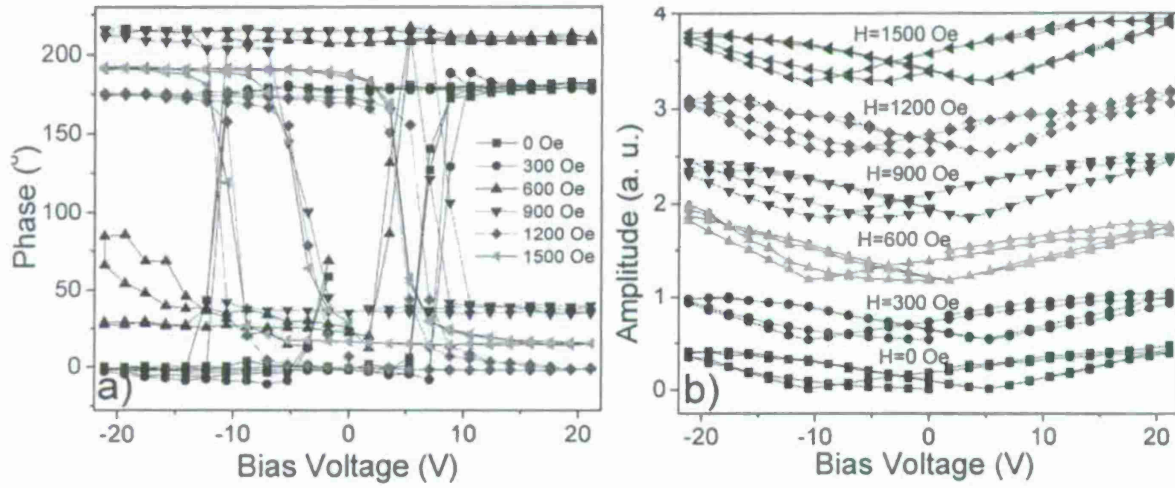


Figure 5. Phase (a) and amplitude (b) curves of the piezoresponse of the PTO-NFO bilayered structure under different magnetic fields. In Figure 2b the plots have been translated vertically to increase their visibility

When the ac electric field is applied through the conductive tip, the ferroelectric layer will start vibrating at the same frequency as a result of the converse piezoelectric effect. The characteristic amplitude at which the electrostrictive layer vibrates is proportional to the piezoelectric coefficient  $d_{ij}$ :  $A = \delta d_{ij} V_{ac}$  (2). In Eq. (2) the constant  $\delta$  is the sensitivity of the optical detector; that is a proportionality factor that accounts for the amplitude enhancement at the tip-sample resonance, whereas  $V_{ac}$  is the testing voltage. From the magnetic field-induced piezoelectric deformation of the samples we calculated the values of the transversal piezoelectric coefficient  $d_{31}$ . These are 25.9, 36.7, 39.8, 45.7, 54.7 and 59.6 pm/V for a magnetic field of 0, 300, 600, 900, 1200 and 1500 Oe. It can be inferred that the transversal piezoelectric coefficient increases linearly with the magnetic field, with a positive slope reaching a maximum value at 1500 Oe, which corresponds to the saturation field of the nickel ferrite layer [7]. The ME coupling coefficient is conventionally defined as  $\alpha_{ME} = \frac{\partial E}{\partial H}$  (5), where  $E$  and  $H$  denote the electric and magnetic fields. The polarization in a dielectric material is proportional to the electric field  $P = \epsilon_{31} E_3$  (6) where  $\epsilon_{31}$  is the in-plane component of the dielectric permittivity tensor. In ferroelectrics with a centrosymmetric paraelectric phase, such as  $\text{PbTiO}_3$  the piezoelectric effect may be considered as the electrostrictive effect biased by the spontaneous polarization:  $d_{31} = 2\epsilon_{31} QP$  (7), where  $Q$  is the electrostrictive coefficient. By combining equations (5), (6) and (7) we obtain the mathematical relationship which allows the quantitative determination of the direct ME coupling coefficient for any type of connectivity scheme between the two constituent phases from the variation of the of the piezoelectric coefficient with the magnetic field:

$$\alpha_{ME} = \frac{1}{2\epsilon_{31}^2 Q} \frac{\partial(d_{31})}{\partial H} \quad (8)$$

By using the bulk value for the dielectric constant ( $\epsilon \approx 1200$ ) [8] of  $\text{PbTiO}_3$  we obtained values of the ME coupling coefficient of 435.3 mV/cm·Oe for the  $\text{PbTiO}_3\text{-Ni}_{0.66}\text{Fe}_{2.34}\text{O}_4$



bilayered nanostructures, respectively. The obtained values are in line with those reported in the literature for particulate perovskite ferrite ME nanocomposites [9-11] indicating a very good coupling between the PTO and the ferrite layers in our nanocomposites. Since the mechanical stress  $\sigma_3$  in a piezoelectric material is defined

as [12]:  $\sigma_3 = \frac{-E_3}{g_{31}}$  (9) and  $g_{31} = \frac{d_{31}}{\epsilon_{31}}$  (10), where  $g_{31}$  and  $d_{31}$  and piezoelectric coefficients, by combining (8) with (9) and (10) we obtain:

$$\alpha_{ME} = -\frac{\sigma}{\epsilon_{31}} \frac{\partial(d_{33})}{\partial H} \quad (11)$$

which is the expression proposed by Vopsariu *et al.* [13]. This shows that our equation and that obtained by Vopsariu *et al.* are equivalent, which furthermore validates furthermore the proposed model for the quantitative and qualitative measurement of the ME coupling coefficient from magnetic field-assisted PFM measurements.

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- 28) "Synthesis and sensing investigation of new coordination compounds nanowires", Kun Yao, Zhijie Li, and Weillie Zhou, The 3rd International Conference on One-dimensional Nanomaterials, December 7-9, 2009, Atlanta, Georgia.
- 29) "In-situ E-beam Nanolithography for Nanodevice Fabrication", Weillie Zhou, Annual Conference of Chinese Electron Microscopy Society, July 16-19, 2009, Zhengzhou, China.
- 30) L. Malkinski, "Magnetic heterostructures with convoluted architectures" (invited) 7<sup>th</sup> Workshop on Multifunctional Materials, Gamboa, Panama Aug. 4-9, 2012
- 31) N.B. Simhachalam and L. Malkinski, "Magnetolectric effect in AlN/CoFe bi-layered thin film composites", 56<sup>th</sup> Annual Conference on Magnetism and Magnetic Materials, Oct 30- Nov 3, 2011, Scottsdale, AZ



32) S. Min, J. H. Lim, J. Gaffney, K. Knittle, J.B. Wiley and M. Malkinski, "Fabrications of scrolled magnetic thin film patterns", 56<sup>th</sup> Annual Conference on Magnetism and Magnetic Materials, Oct 30- Nov 3, 2011, Scottsdale, AZ

33) L. Malkinski, M. Yu, D. J. Scherer II, "Magnetic interactions in 2-dimensional arrays of magnetic stripes", presented at Materials Research Society Meeting Spring 2010, San Francisco, Ca.

34) L. Malkinski, M. Yu, D. J. Scherer II, "Microwave absorption of magnetic antidote arrays", presented at Materials Research Society Meeting Spring 2010, San Francisco, Ca.

35) L. Malkinski, "Microwave properties of magnetic nanostructures", Seminar at the University of Wyoming, Laramie, WY, March 6, 2010

36) L. Malkinski, "Voltage control of magnetism in multiferroic composites", Seminar at the Colorado State University, Fort Collins, Co. March 7, 2010

37) L. Malkinski, "Voltage control of magnetism in multiferroic composites", Seminar at the University of Colorado at Colorado Springs, Colorado Springs, Co. March 8, 2010

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14. ABSTRACT  Report is a summary of the overall project objectives which include: <ul style="list-style-type: none"> <li>• Develop a synthetic technology of lead-free high frequency multiferroic Composites;</li> <li>• Develop a method of fabrication of arrays of free-standing magnetoelectric or multiferroic composites;</li> <li>• Investigate wet chemistry synthesized multiferroic nanomaterials (nanoparticles, nanowires, nanotubes, etc.) using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to study their correlation between morphologies, composition, assembly, etc. and synthesis conditions. Meanwhile, in-situ nanolithography has been developed for multiferroic related devices fabrication;</li> <li>• Fabricate spinel and perovskite pristine phases with controllable composition and dimensionality and use them as building blocks to design magnetoelectric ceramic nanocomposites with integrated functionalities;</li> <li>• Demonstrate that the direct ME effect can be measured at nanometer-length scale by detecting the changes in the piezoresponse of a multiferroic material when subjected to the action of a magnetic field;</li> <li>• Mapping of the ME coupling through the domain imaging;</li> <li>• Estimate quantitatively the ME coupling coefficient;</li> <li>• Understand the fundamental physics of magnetoelectric interactions at nanoscale for implementation of multiferroic materials into functional devices.</li> </ul>					
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